

AN OVERVIEW OF THE SHELL FLUOROAROMATICS PLANT EXPLOSION

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The consequences and cause of a runaway reaction during the production of difluoro-nitrobenzene are described. A previously unknown reaction, resulting from contamination of recycled solvent by an unforeseen route, heated the reactor contents to a temperature at which they decomposed in a violent second reaction. Lessons for safety assessment during batch reaction development and design are highlighted.

KEYWORDS: Fluoroaromatics, batch, reaction, explosion, runaway, contamination.

INTRODUCTION

On 20th March 1990, the halogen exchange reactor of the Stanlow Fluoroaromatics Plant was ruptured by the pressure generated by a runaway reaction during the production of 2,4 difluoronitrobenzene (DFNB) from 2,4 dichloronitrobenzene (DCNB) during the manufacture of 2,4 difluoroaniline (DFA). The blast from the rupture was enhanced by the formation of a fireball when the reactor contents ignited within the plant structure. Six operators were injured, one of whom died three weeks later from post-operation complications following lower-limb surgery. The plant itself was partially demolished and there was blast and missile damage up to 500 metres away.

DIFLUOROANILINE PROCESS

There are two reaction stages, separated by a batch distillation, as shown in Figures 1 and 2. The first ("halex") reaction is a nucleophilic aromatic substitution in which chlorine atoms, activated by an electron withdrawing nitro group in the ortho or para position, are displaced by fluorine by reaction with potassium fluoride in a polar aprotic solvent. The solvent in the Stanlow plant was dimethylacetamide (DMAC). The reaction is accelerated by the addition of a phase transfer catalyst such as tetramethyl ammonium chloride (TMAC).

The potassium chloride formed in the halex reaction is subsequently separated from the product mix by centrifugation. The fluorinated compound is separated by batch distillation of the centrifugate, which also includes unreacted feedstock, byproducts, reaction solvent and the toluene used for centrifuge washing.

The second reaction stage is hydrogenation of the nitro group to form DFA.

"HALEX" REACTION

15 tonne (total charge) halex reaction batches were made in a stirred reactor (Figure 3) on a multi-purpose fluoroaromatics plant originally designed for the production of 3-chloro 4-fluoroaniline (CFA). DMAC was pressured in from a weigh vessel together with the catalyst TMAC, potassium fluoride powder was loaded from drums, and finally DCNB was pumped in. The reactor was heated up to 165 Deg C over 3 hours and held at this temperature for a further 14 hours. The heat of reaction (-33kJ per halogen exchanged) was removed by a pressurised water jacket system. The reactor contents were then cooled, neutralised with sodium bicarbonate and pressured with nitrogen to centrifuge feed vessels.

The pressure in the reactor was controlled throughout the reaction at about 0.2 barg by a split range controller which either admitted nitrogen or vented to the plant vent header. Build-up of pressure had never been observed during any CFA or DFA halex reaction during the 14 years the plant had been in operation. A remotely-operated vent valve also discharged into the same vent line, which contained a restriction orifice to prevent possible high venting rates (eg after nitrogen-pressured transfers) from overloading the vent header. The reactor was fitted with a relief valve set to relieve to atmosphere at 5 barg and sized for what had been calculated to be the worst case - a utility failure during the production of another fluoroaromatic.

DFNB DISTILLATION

The halex reaction product was centrifuged to remove solids, mostly potassium chloride and fluoride. The centrifuge cake was washed with toluene which was also the azeotroping agent for removal of water in the first stage of the subsequent distillation. The product and washings were fed to holding vessels V4 and V6 (See Figure 4). The contents of these were filtered to remove any remaining solids and transferred to the batch distillation still vessel V7 when and as required. Periodically water was circulated, to remove salt deposits from the holding vessels and their associated filters, and disposed of to a holding vessel and subsequent biotreatment.

The distillation column C1 was packed with Sulzer Mellapak and operated batch-wise between 200 and 25 mbara to separate the contents of V7 into fractions as follows: (See Figure 4)

<u>Cut</u>	<u>Pressure</u> (mbara)	<u>Temperature</u> (deg C)
(1). A toluene/water azeotrope to remove water.	200	76
(2). 'Dry' toluene for re-use.	-	-
(3). A toluene/DMAC intercut for redistillation.	-	-
(4). DMAC for reuse in the halex reaction.	100	110
(5). A DMAC/DFNB intercut for redistillation.	-	-
(6). DFNB for hydrogenation.	50	125
(7). Monofluorinated chloronitrobenzene (CFNB) for recycle.	-	-
(8). Heavy residues for third party incineration.	-	-

Control of the 'cut' between fractions was by continuous monitoring of specific gravity changes in the overhead stream, confirmed by plant laboratory GC analysis.

The normal procedure was to refill V7 after stages 1-4, repeat these stages and then continue with stages 5-8.

EVENTS LEADING UP TO THE EXPLOSION

A DFA production run had been in progress since November 1989 and, by the beginning of March 1990, 40 hallex batches had been made without incident. From the plant records and the statements of operating personnel it was possible to make a detailed reconstruction of the subsequent routine and non-routine events and of the various movements of material between plant vessels. This was vital to the elucidation of the incident.

On the 2nd March, a very large quantity of water entered V7 via two passing valves from the centrifuge system, which was being routinely washed to remove accumulated salts. The contents of V7 were moved to holding vessels and returned batchwise for water removal by repeated azeotroping. This appeared to be successful but, when the distillation sequence was continued on the 10th March, 1% water was found in the DMAC/DFNB intercut and the nominally DFNB product stream obviously contained another compound, later shown to be dimethylamino fluoronitrobenzene. The distillation column contents were therefore drummed off for disposal. Various samples were taken for later examination and proved invaluable for the explosion investigation. Between the 10th and the 19th of March similar attempts to recover product from the remaining contents of the various holding vessels were unsuccessful but apparently on-specification DMAC was recovered to storage for use in the next hallex batches.

Hallex batches 41 and 42 used DMAC recycled before the water incursion to the distillation section and the product quality and yield were normal. The DMAC used for hallex batch 43 contained some material recycled after the water incursion, but there was nothing unusual about the reaction and the product was normal. However, all the DMAC used for batch 44 was recovered after the water incursion. This batch was charged on the 19th March and heated up normally. When it reached 165 Deg C, the temperature continued to rise and the operating crew continued reducing the jacket temperature. They had not seen that there was an abnormal and rising pressure on the reactor because pressure was not shown on the VDU display they were using at the time. The outside operator alerted his colleagues to the abnormally high pressure, the relief valve lifted and, before they could take further action, the reactor exploded.

CONSEQUENCES OF THE EXPLOSION

The reactor was torn into three large pieces one of which was thrown 200 metres. Almost all the other missiles which fell outside the immediate area landed between NNW and NW of the reactor. The reactor itself became virtually a straight piece of metal, the plant structure within about 5 metres was either turned into missiles or buckled beyond recognition and the surrounding structure collapsed. (See Figure 5). Off-plot blast damage was erratic, suggesting shielding or an asymmetric event. In Thornton Research Centre, 300 - 500 metres to the east, there was random damage, mainly windows cracked and broken, and doors and panels displaced.

Witnesses report that the reactor contents formed a fire ball. This started local fires and initiated what became a major conflagration in an adjacent unit where vessels containing xylene were damaged by the blast and/or missiles. The various fires took about four hours to extinguish but the County and Shell fire fighters were able to prevent further spread.

The three process operators on the Fluoroaromatics Plant and three on an adjacent plant were injured and evacuated to hospital. One died three weeks later of post-operation complications following lower limb surgery.

NATURE OF THE EXPLOSION

The reactor process conditions were recorded as one minute averages by the plant computer but only transferred to "hard" disc storage at 5 minute intervals. After the explosion the disc was recovered but it only showed the one minute interval spot readings upto the end of the last complete 5 minute interval before the explosion. The reactor pressure and temperature and the jacket temperature are shown pictorially in Figure 6. This indicates a typical runaway reaction, but other possibilities were systematically investigated and have been eliminated.

The Combustion and Fuels Department of Shell - Thornton Research Centre were able to make immediate and accurate measurements of much of the damage on Stanlow and on their own site. They will be reporting their detailed findings and conclusions elsewhere. These may be summarised :-

The event started within the vessel which ruptured at a pressure of 50 - 100 barg. The small number of reactor fragments and the blast damage pattern indicate that there was not a detonation. The level of blast damage, especially within Thornton Research Centre, was too great to be accounted for by the vessel rupture alone. However, witness reports and damage to a nearby light fitting indicate that there was a fire from a leak immediately before the rupture. It is postulated that the vessel contents, having been projected into the obstructed space of the reactor structure, were ignited and formed a very energetic, highly congested jet fireball. This would account for the overpressures deduced from the

damage and for the blast pattern which indicates a long duration pressure pulse (> 100ms), with a slow decay and equivalent over-pressure and rarefaction under-pressure stages. It also explains why the major vessel fragment was projected to the northwest.

ORIGINAL PROCESS DEVELOPMENT

The Stanlow Fluoroaromatics Plant was originally designed in 1975 for CFA and was modified subsequently for the production of other fluoroaromatics including DFA. The original halex solvent was dimethyl sulphoxide (DMSO), but DMAC was used for all products after 1981, primarily to allow the separation of DFNB from solvent in the distillation column. This change also eliminated stress corrosion cracking which had been a major problem with DMSO in the halex equipment. DMAC was chosen in preference to dimethyl formamide (DMF) because of literature references to and Shell experiences of the formation of highly unstable mixtures of DMF and halogenated hydrocarbons or nitrocompounds.

In 1980/ 81, optimum reaction conditions for DFNB were established using DMAC and tests made to confirm the absence of thermal instability under higher than normal process temperatures.

(i) Build-up of impurities - Gas Chromatographic analysis showed that no organic impurities built up in the recycle toluene and DMAC after 10 reaction/distillation cycles. Even acetic acid, which might have been formed by hydrolysis of DMAC by the water in the reaction medium, was not detected. No effects of solvent recycle were seen in the following halex batches.

(ii) Stability at reaction conditions - storage of the organic layer of the reaction product mixture, with and without 1000 ppm of iron powder at 150 Deg C and atmospheric pressure, (reaction conditions at the time), gave no change in composition.

(iii) Thermal stability - experiments with the adiabatic Sikarex 3 calorimeter were carried out on :

- filtered reaction mixture with 1000 ppm iron powder for 20 hours at 180 Deg C. There was no exotherm but some DFNB and DMAC decomposed to heavy ends.

- DFNB distillation residues. There was some exothermic decomposition at a slow rate at 200 Deg C. Heat evolution was measured as 48 kw/tonne which could be absorbed in the distillation.

(Note that this work was carried out before 1982, after which Shell modified the standard Sikarex equipment to provide, inter alia, for testing stirred reacting non-homogeneous mixtures.)

After 1982 no DFA was made until 1989. Before this production run started, a matrix of reaction temperature and composition conditions were evaluated on a laboratory scale and the reaction was optimised at 165 Deg C (of the original temperature of 145 Deg C) to increase

throughput. Because stability testing had already been carried out at 180 Deg C no further work was considered necessary.

CHEMICAL REINVESTIGATION

Initially, no obvious initiating cause of the temperature runaway and subsequent explosion could be established, but analysis of various samples had identified the presence of acetic acid in the plant vent system and in the distillation intercut vessels and that nominally DFNB product contained significant quantities of dimethylamino - fluoronitrobenzene. A programme of work was then carried out to re-examine the chemistry and stability of the halax reaction and halax product distillation systems and the effects of identified and possible contaminants (eg water) and recipe variations. Acetic acid was included in the list of contaminants for examination.

This work was carried out at the Shell Group Central Laboratories in Amsterdam. Both the calorimetry and the reaction chemistry will be more fully reported at the 13th International Symposium on Fluorine Chemistry, Sept 1-6, 1991, Bochum (FRG).

Shell modified Sikarex equipment, with magnetic stirring and improved monitoring and controlling software, was used to determine the thermal stability of a range of reaction mixtures, reactants, solvent and possible contaminants. A Mettler calorimeter was used to determine accurate heat data and the reaction was simulated using a computer model. The original development work was confirmed. No reactions were found that could explain the incident apart from the effect of acetic acid in the halax reaction. This was shown to cause an exothermic reaction, which lifts the reactor temperature rapidly from 160 to 240 deg C. At this temperature a second runaway reaction occurs, with extremely rapid temperature and pressure increases, due to the decomposition of DFNB/DCNB. The temperature profile of the runaway batch could be repeated exactly with the appropriate addition of acetic acid. (Figure 7) The gas evolved was identified as mainly ketene and carbon dioxide. Ketene, being flammable, could account for the flames which were seen before the explosion. It is hydrolysed by water to acetic acid which would explain the discovery of the latter in the vent system.

(It is noteworthy that when acetic acid had been used in the development of an analogous halax reaction during another Shell Research programme, it had been found to inhibit the reaction completely at the low concentrations used.)

Chemical and physical experiments were carried out to determine how acetic acid could have been formed and recycled to the halax reactor. DMAC is known to react with water to form dimethylamine and acetic acid, but the four component system equilibrium strongly favours DMAC. It was shown that with water alone at 160 Deg C there is no detectable hydrolysis of DMAC but if DFNB is present this acts as a 'scavenger' for dimethylamine so shifting the equilibrium. (See Figure 8). In the presence of toluene negligible hydrolysis takes place. This would be the case while water is removed in an azeotropic distillation.

However, it was also shown that a massive water incursion would have led to the formation of two phases in the unmixed distillation still vessel V7. Initially some of the aqueous upper layer would probably not have been circulated from V7 to the column and so water would have remained in the system to react with DMAC during the higher temperature stages of the distillation.

Further work confirmed the existence of a DMAC-acetic acid azeotrope with a similar boiling point to DMAC, which would have been recycled with the DMAC to the storage tanks under the distillation conditions. Finally, it was shown that all the fractions distilled from this DMAC-acetic acid mixture contained between 0.5 and 4.5% water, suggesting a possible ternary azeotrope and indicating that water would not be fully separated by simple distillation once acetic acid had been formed.

The reaction of acetic acid with the halox reaction components was investigated. Initially acetic acid and KF react to form potassium acetate, which in turn reacts with DCNB to form an acetoxy-chloronitrobenzene. This is not stable under the reaction conditions and reacts further to give decomposition products among which are ketene, carbon dioxide, polyaryl ethers and tars. (See Figure 9). This reaction was not previously known but was successfully simulated in a laboratory experiment. There is no literature precedent. The quantity of gas generated during the actual runaway reaction has been estimated from the reactor pressure record to match the gas generated experimentally with 0.5 mole acetic acid per mole of DFNB. This is of the same order of magnitude as the ratio of acetic acid to DMAC found in the fire-water contaminated DMAC charge vessel under the debris after the explosion.

From the plant records and the various analyses it has been shown that all the water was not removed with the toluene. Both acetic acid and water remained in the intercut vessels and were found in the recycle DMAC samples. The operators were unaware of their inability to remove all the water once acetic acid had been formed.

Analysis of the samples of DMAC taken from the plant after the explosion indicates that enough acetic acid had entered to cause the incident as observed.

The consequences of stirrer failure, an alternative explanation, were simulated theoretically in a computer programme which predicted a runaway but only at half the rate actually observed even under worst (perfectly adiabatic) conditions. All available physical evidence indicates that the stirrer did not fail.

GENERAL LESSONS

Procedures for assessing the potential for runaway reactions should recognise:

- the need to routinely and selectively re-evaluate established processes in the light of new knowledge and techniques, identifying priority items for detailed examination. (Shell has had such procedures for many years, carrying out technical safety reviews and Hazops on older plants. Unfortunately, it is impractical to cover all aspects, and high quality, sound initial training and regular updating of the technical staff involved are essential.)
- the need to identify all plausible impurities in recycle streams during the development of new processes or the re-examination of old ones, to test their effect on reaction stability, and to develop and use suitable analytical methods to detect them under plant conditions.
- the consequences of deviations from standard reaction conditions which would invalidate any presumption that known dangerous conditions could not be achieved (eg increasing a reaction temperature and so closing a "safety gap" provided by limited heat input).

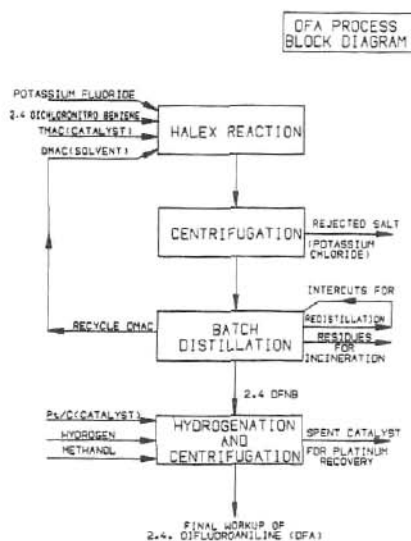


Figure 1 DFA process block diagram

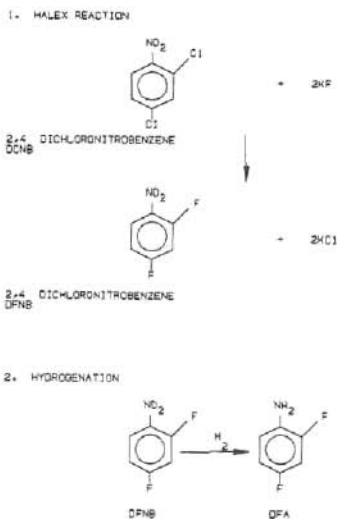


Figure 2 DFA process reactions

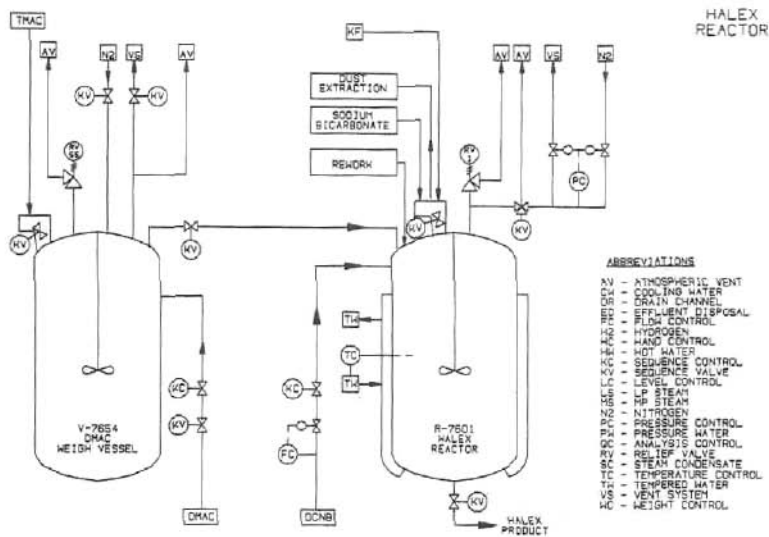


Figure 3 Halex reactor flowscheme

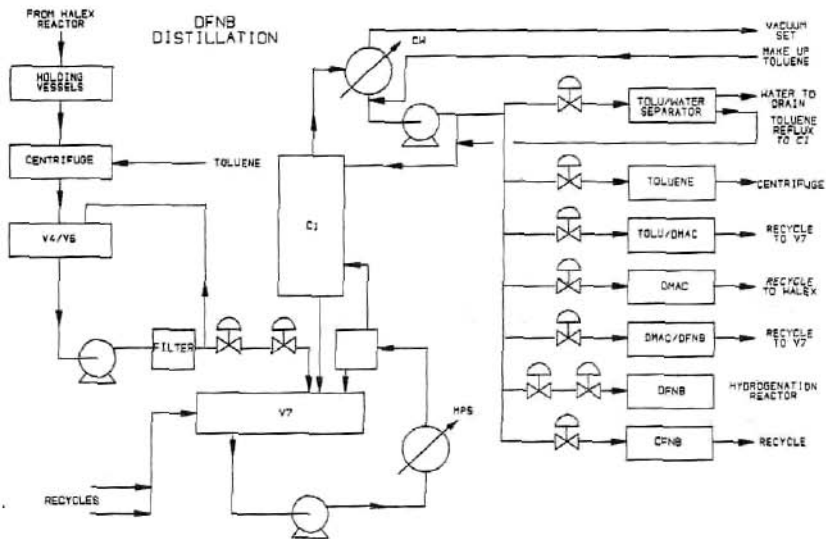


Figure 4 DFNB distillation

2,4 - DFNB Batch 44
Stanlow 20 March 1990

Figure 6

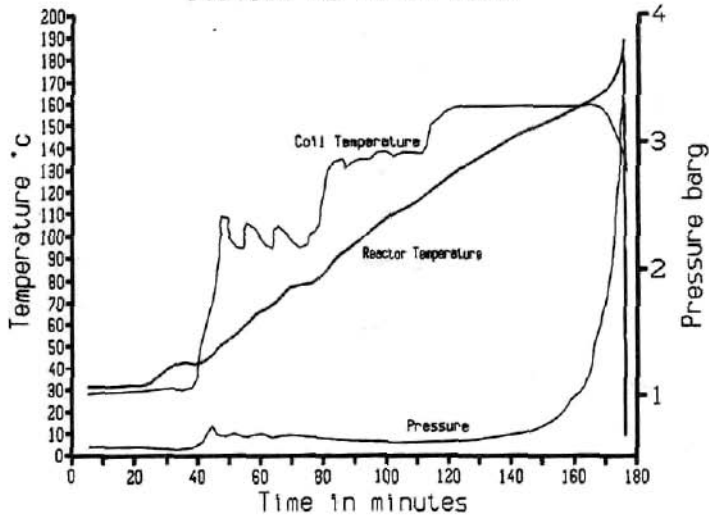


Figure 6 Process conditions - DFNB runaway batch

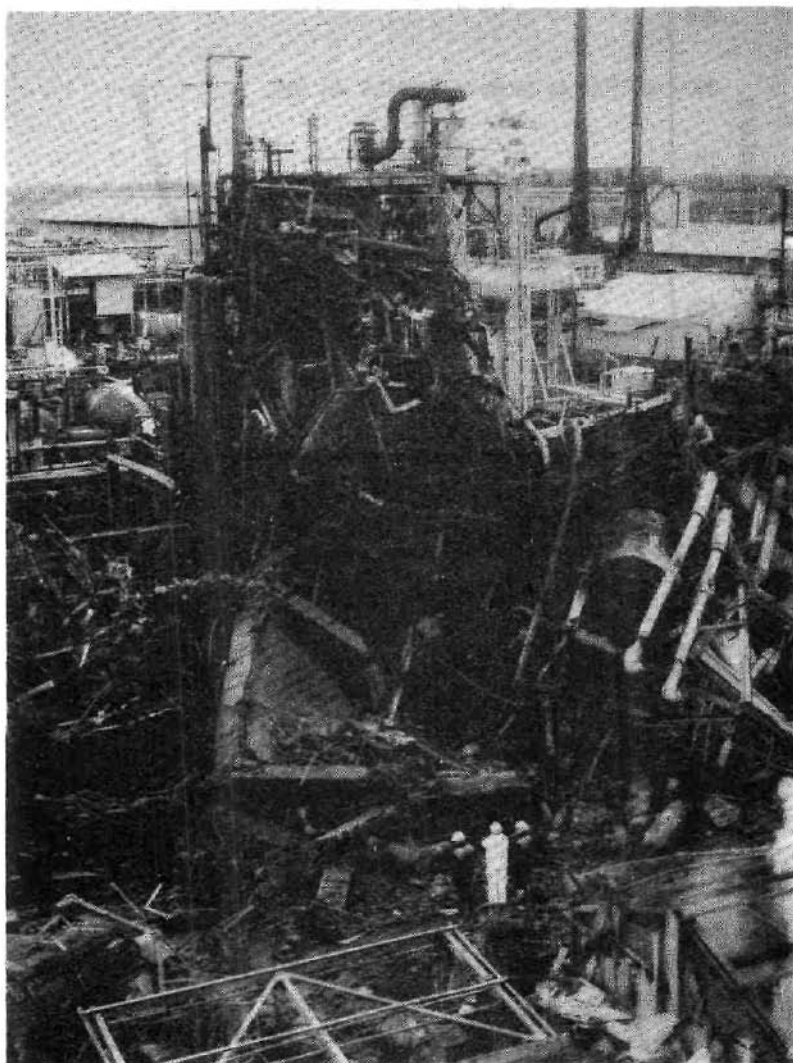


Figure 5 Fluoroaromatics plant after explosion

THERMAL STABILITY INVESTIGATION
CP17660 Data Versus Batch 44 Data

Figure 7

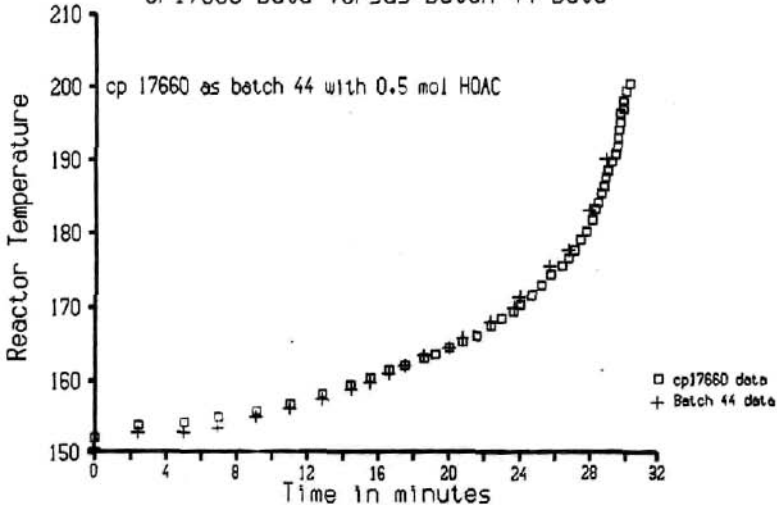


Figure 7 Laboratory simulation of runaway batch conditions

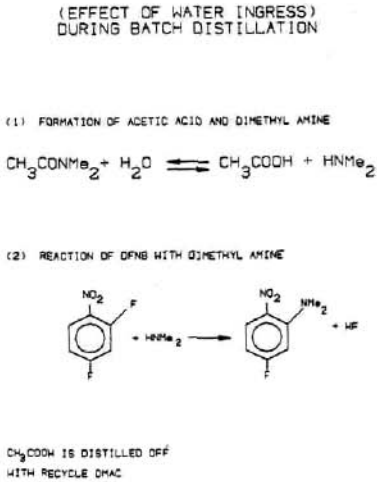


Figure 8 Water in DFNB distillation

EFFECT OF ACETIC ACID IN HALEX:
POSSIBLE MECHANISMS

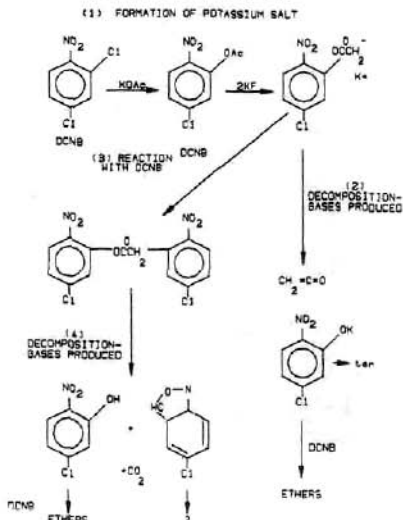


Figure 9 Acetic acid in "halex"